

APPENDIX B

RECEIVING WATERS

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1.0 GOALS AND PURPOSE OF THE APPENDIX

The primary goal of this appendix is to outline the rationale and methods to characterize water quality in and around a proposed mine site. It is intended to be used in conjunction with other appendices in this source book to which the reader is referred for more detailed information. Relevant appendices include Appendix A, *Hydrology*, Appendix E, *Wastewater Management*, Appendix F, *Solid Waste Management*, and Appendix H, *Erosion and Sedimentation*. Background materials in this appendix review how mining activities can impact water quality, describe how water quality standards are developed, outline general processes related to contaminant dispersal, and summarize important aspects of a watershed-based evaluation. The background materials are followed by a section that describes practical aspects of developing a program to monitor water quality. A section on data analysis provides general information for modeling water quality data. The appendix concludes by reviewing the important aspects of monitoring and quality assurance as needed for NEPA (EIS) and NPDES purposes.

Surface and ground waters that receive treated and untreated discharges from mine sites are referred to as “receiving waters”. Point source discharges to receiving waters are regulated under Section 402 of the Clean Water Act, which requires the preparation of National Pollutant Discharge Elimination System (NPDES) permits. A key aspect of the NPDES permitting process is protecting the quality and designated uses of receiving waters. To predict the potential impacts of mining operations on receiving water quality, it is important to have adequate discharge and baseline receiving water data. Because data needs are varied and many, it is important to assess the scope of specific water quality data needs and their uses prior to beginning data collection to ensure that data will serve all intended purposes and that they will be collected in an efficient manner. Receiving water quality data at mines may be used for a variety of other purposes including:

- Establishing baseline conditions to support calculations of NPDES permit limits,
- Providing justifications for site-specific criteria,
- Developing dissolved to total recoverable translators,
- Developing the basis for effluent trading,
- Documenting the quality of the affected environment for NEPA analysis,
- Determining cumulative impacts under NEPA,
- Predicting environmental consequences of the proposed action and alternatives under NEPA,
- Assisting in conducting watershed analyses,
- Supporting remedial activity in impaired watersheds, and
- Monitoring long-term trends.

This guidance is focused on characterizing water quality at proposed mines. Although the term “receiving water” is used throughout, the methods and techniques described can be applied to any surface or ground water and are not restricted to waters that will receive direct discharges of mine effluent. As part of this analysis applicants may be required to understand the interactions between surface and ground waters and characterize other physical and biological

aspects of the aquatic environment. The concepts and guidance presented herein also are appropriate for surface water and ground water quality monitoring at other stages of a mine's life cycle, including operation, closure, and post-closure. In these settings, water quality data can be used for compliance monitoring, trend monitoring, monitoring the effectiveness of Best Management Practices (BMPs), and establishing and verifying any permitted mixing zones.

In 1997, EPA released the "Hardrock Mining Framework", a document that outlined the Agency's approach to dealing with environmental concerns at hardrock mining sites. This document acknowledged that recent national initiatives were directed toward ensuring that point sources of pollution were addressed on a watershed basis. In addition, the Framework recognized that the watershed approach could be an administrative means to reduce pollutant loadings on a cost-effective basis. Consequently, this appendix stresses the use of the watershed approach to determine receiving water quality.

2.0 REGULATORY AND TECHNICAL BACKGROUND FOR DESIGNING A WATER QUALITY ASSESSMENT PROGRAM

This section briefly discusses technical and regulatory factors that are important to consider when designing a program to assess water quality. It begins by describing the types of water quality impacts that can occur as a result of mining activities, then briefly summarizes the regulatory development of water quality standards, describes processes that affect contaminant dispersal, and discusses the watershed approach to water quality assessment. Applicants proposing new or expanded mining projects should be certain to fully characterize the existing quality of surface and ground water resources at their site, so that an EA or EIS will be able to fully describe the types of impacts that the mine may create.

2.1 Mining Impacts on Water Quality

For the purposes of considering impacts to water quality, the diverse activities associated with hardrock mining can be divided into four main areas. *Disturbance* activities include the development of mine pits, shafts, and adits and surface disruptions associated with mine development and facility construction (e.g., grading, road construction, impoundment construction, foundation preparation, soil stripping, and pipeline and powerline construction). *Processing* activities include the construction and operation of crushing and milling facilities; flotation concentrators; smelters and refineries; heap and dump leach facilities; vat and tank leach plants; water treatment facilities; and carbon stripping, zinc precipitation, and solvent extraction/electrowinning plants. *Waste disposal* activities include the construction and operation of waste rock dumps, overburden piles, tailings impoundments, and slag piles and other process waste. *Support* activities include those actions required for day-to-day operation of the mine such as equipment maintenance, fuel storage, wastewater treatment, and laboratory analysis. EPA has prepared a series of Technical Resource Documents that summarize the extraction and beneficiation of lead-zinc, gold, copper, iron, uranium, gold placer, and phosphate and molybdenite ores. They can be obtained from the EPA Office of Solid Waste webpage (<http://www.epa.gov/epaoswer/other/mining.htm>).

2.1.1 Disturbance Activities

Disturbance activities increase the potential for surface or ground water impact by exposing mineralized rock, disturbing native soils and vegetation, altering slope angles, and modifying watershed and aquifer characteristics. Mine pits, adits, shafts, and open cuts that expose mineralized rock have the potential to produce increased loadings of metals, dissolved solids, suspended solids, and acidity to surface waters. The construction of roads, utility lines, and facility foundations and stripping activities associated with the development of mine pits and the construction of mine processing, disposal, and water management facilities increase the potential for sediment contamination. These activities alter natural watershed characteristics by increasing runoff, decreasing soil cohesion and infiltration, and increasing susceptibility to erosion. Potential mining impacts associated with erosion and sedimentation are described in more detail in Appendix H, *Erosion and Sedimentation*.

The types of constituents that can be released during or following disturbance activities depend on the nature of the mineralization and the mining operation. Mining disturbances may increase the concentrations of suspended particles and metals (e.g., Al, As, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Se, Ag, Zn), major cations (e.g., ammonia nitrogen, Ca, Mg, K, Na), and anions (e.g., nitrate, sulfate, chloride, carbonate) that form a large portion of the total dissolved solids in surface waters. Constituent concentrations can be increased through dissolution or retransport of naturally occurring compounds or by the dissolution of reagents, such as blasting residues (Table B-1), that are used during disturbance activities. Importantly, surface and underground disturbances can result in the production of acid drainage. This phenomenon, referred to as acid mine drainage or acid rock drainage, results when iron sulfide minerals (pyrite and marcasite), which commonly occur in mineralized zones, are exposed to the oxidizing environment of the atmosphere. The acidity produced from exposed pit walls and underground workings can impact surface water quality for many years after mining ceases by lowering pH and increasing the amount of metals leached from exposed surfaces and maintained in solution.

Disturbance activities release contaminants to surface and ground waters primarily through precipitation runoff, releases of mine water, or disruption of aquifers and their confining layers.

2.1.2 Processing Activities

Processing activities increase the potential for surface water impact by creating facilities in which metals are concentrated to values significantly above those in the ore, dissolving metals into solution, grinding metal-rich ore into fine particle sizes, and storing and using large quantities of reagents that can potentially degrade surface water quality. Depending on the type of milling and concentrating process employed, a mine may construct ore stockpiles to assure consistent feed to a mill. Pad and dump leaching facilities have associated impoundments to store barren and pregnant leach solutions, pipelines to transfer solutions between storage ponds and leach pads, and leachate and seepage collection facilities.

Contamination from processing facilities can occur in many forms that depend on the type of ore being processed, the type of on-site processing, and the specific mine design. Consequently, the list of chemicals used at a mine site can be extensive and may include flotation reagents, frothing and collection agents, scale inhibitors, flocculents, thickeners, leach solutions, and leachate neutralizing solutions. Table B-1 gives examples of the types of processing reagents that may be used by mining operations; it should be recognized that this table does not provide a comprehensive listing.

Processing activities can release contaminants to surface waters in a variety of ways that include spills of reagent materials or processing fluids (e.g., pipeline ruptures), leaks at processing facilities (e.g., liner tears), storage pond overflows (e.g., during storm events), and facility failures (e.g., slope failure of a leach dump). Contaminant pathways can be direct (release directly to surface waters) or indirect. Examples of indirect contaminant pathways include infiltration to ground water that exchanges with surface water, seepage to soil or bedrock which discharges to surface water, and seepage through or below impoundment dams and berms.

2.1.3 Waste Disposal Activities

Waste disposal activities increase the potential for surface water impact by creating permanent features in which waste materials are stored. Waste materials can serve as sources of leachable metals, acidity, cyanide or other toxic constituents, and fine-grained sediment for many years after mining ceases. Examples of these facilities include waste rock dumps, impoundments, and spent ore piles. Descriptions of the types of waste disposal facilities used at mines sites are given in Appendix F, *Solid Waste Management*.

Waste disposal facilities can impact receiving waters through the release of sediment, metals, and other contaminants. In part, the types of contaminants available to the environment depend on the character of the waste materials (e.g., grain size and mineralogy), the means by which these materials were processed (e.g., cyanide or acid leach), and the types of closure procedures that were employed (e.g., rinsing, neutralization, capping and revegetation). Fine-grained materials such as tailings piles are a significant source of erodible sediment that potentially can be mobilized and redeposited in stream beds by surface runoff. Over the long term, waste rock dumps, tailings impoundments, and spent ore piles that contain sulfide-bearing material can contribute acidity to receiving waters through the oxidation of pyrite and marcasite as described in Appendix F, *Solid Waste Management*. Acid leachates produced from these materials facilitate the dissolution of the metals listed in Section 2.1.1, *Disturbance Activities*. Closed cyanide and acid heap leach units may contain residual cyanide and cyanide by-products, or acidity that can be released to receiving waters if the heaps are not properly rinsed and neutralized (Simovic et al., 1985).

Contaminants can be released to surface waters in a variety of ways that include physical failure (e.g., breach or sloughing of a tailings impoundments), seepage (e.g., below an impoundment dam), saturation and overflow of lined facilities (i.e., the “bathtub” effect), and erosion by wind and water (e.g., gully formation during storm events). Contaminant pathways can be direct (release directly to surface waters) or indirect. Examples of indirect contaminant

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Table B-1. Example Reagents Used at Metal Mines

Disruption Activities		
Blasting Agent	Ammonium nitrate & fuel oil (ANFO)	
Processing Reagents		
Flotation Reagents	Alkaline sulfides Sodium cyanide Sodium ferrocyanide Aliphatic alcohol Phenol Ethyl and amyl xanthates Alkyl dithiophosphate Methyl isobutyl carbinol Aerofloats Copper sulfate Zinc sulfate Sodium sulfide Kerosene	Phosphorous pentasulfide Sulfuric acid Sodium hydroxide Pine oil Polyglycol ether Sodium isopropyl xanthate Sodium diethyl phosphorodithioate Thiocarbamate Pine oil Dichromate Zinc hydrosulfate Sodium bisulfate
Solvent Extraction - Electrowinning Reagents	Sulfuric acid Oxime compounds Amphoteric fluoroalkylamide derivative	Hydrocarbon distillates Cobalt sulfate solution Diethylene glycol butyl ether
Miscellaneous Concentrator Reagents	Anionic polyacrylamide Polyacrylate	Polyphosphate Polymeric and organophosphorous compounds
Leaching Reagents	Sulfuric acid	Sodium cyanide
Leach Processing Reagents	Sodium hydroxide Hydrochloric acid Nitric acid	Lead nitrate Zinc Sodium sulfide
Leach Neutralizing Reagents	Hydrogen peroxide Chlorine Sodium hypochlorite	Lime Sulfur dioxide Copper
Support Activities		
Petroleum Products	Gasoline Diesel fuel Gear oil, motor oil, hydraulic oil Lubricating grease and oil	Antifreeze Paraffinic, naphthenic, and aromatic hydrocarbons (solvent) Propane
Wastewater Treatment Reagents	<u>Ion Exchange Regenerants:</u> Hydrochloric acid Sulfuric acid Sodium chloride <u>Descalants:</u> Calcium sulfate Calcium carbonate Silicon dioxide Sodium hexametaphosphate	<u>Chemical Precipitation Reagents:</u> Lime Alum Sodium hydroxide Calcium hydroxide Hydrogen sulfide Calcium sulfide
Sources: Coeur Alaska, Inc., 1997; U.S. EPA, 1994a, 1994b, 1994c, 1998a; Knorre and Griffiths, 1985; Montgomery Watson, 1996; Scott, 1985; Viessman and Hammer, 1993.		

pathways include infiltration to ground water that exchanges with surface water, seepage to soil or bedrock which discharges to surface water, and seepage through or below impoundment dams and berms.

2.1.4 Support Activities

Support activities can increase the potential for receiving water impacts through facilities that use and store chemicals and generate waste materials. Support activities can release contaminants to surface waters through a variety of means that include spills and leaks from fuel handling and storage facilities, seepage from solid waste landfills, and seepage and runoff from equipment maintenance facilities. Contaminant pathways may be direct or indirect. Examples of indirect contaminant pathways include seepage to soil or bedrock from above-ground fuel storage tanks and runoff from soils contaminated with solvents or degreasing agents.

2.2 Water Quality Standards

An important aspect of mine review for EPA is evaluating whether a project will adversely affect water quality. One measure of this analysis is the potential to cause exceedances of water quality standards. This type of analysis involves characterizing potential discharges to streams and determining the impacts they would cause to water quality. Prior to evaluating the potential for water quality impacts, the water quality standards that apply to the receiving water must be determined. Water quality standards are provisions of State or Federal law which consist of three components: (1) designated beneficial uses for all Waters of the U.S., (2) water quality criteria (which may be numeric or narrative) for the waters based upon their uses, and (3) antidegradation policies. State water quality standards and implementing provisions are approved by EPA and are codified in State regulations. It is essential for a mine to obtain the most up-to-date state water quality standards and regulations since they often change on a periodic basis. Many of these regulations are now available on-line. More information regarding water quality standards is provided in EPA's Water Quality Standards Handbook (U.S. EPA, 1994d).

Under the Clean Water Act, each State must classify all of the waters within its boundaries by their intended use [see §303(c)(2)]. Once designated beneficial uses have been determined, the State must establish numeric and narrative water quality standards to ensure the attainment and/or maintenance of the use. Designated beneficial use classifications include the use and value of water for public water supplies; protection and propagation of fish, shellfish, and wildlife; recreation in and on the water body; and agricultural, industrial and navigational purposes (see 40 CFR §131.10 for more detail on the designation of uses). For a specific water body, a mine can determine the applicable standards based on the designated use classifications. Where multiple use classifications apply to a water body (e.g., recreational and aquatic life uses), the most sensitive use designations generally apply. Water bodies, especially minor tributaries, may not be identified in State regulations along with their designated beneficial uses. In these cases, States may assign to tributaries the same designated uses as the larger water body that they flow into. Alternatively, they may have a general set of classifications that apply to all unspecified water bodies.

EPA recently published an updated listing of nationally recommended water quality criteria for 157 pollutants (U.S. EPA, 1998b). States may either adopt these criteria or develop alternative criteria that protect the designated uses of their waters. In such cases, the Clean Water Act requires States to use sound scientific rationale to develop their water quality criteria. Criteria may be expressed as constituent concentrations, levels, or narrative statements that represent a quality of water that supports a designated use. Criteria may be developed for acute and chronic toxicity to aquatic organisms, agricultural and industrial uses, and human health effect protection. Criteria, which are developed for both fresh waters and saline waters, may be designated in the form of dissolved, total recoverable, and/or total constituent concentrations. Acute criteria are based on one-hour average concentrations that cannot be exceeded more than once every three years on average, whereas chronic criteria are based on four-day average concentrations that cannot be exceeded more than once every three years on average. While some States use the same water quality standard values for all streams assigned an individual designated use, others depend on stream-specific conditions. For example, some metals are more toxic under low hardness conditions and the applicable standards depend on the hardness of the receiving water. Other standards (e.g., turbidity and temperature) may be based on deviation from natural conditions. For carcinogenic constituents, applicants should check with State authorities to determine the human health risk factors that apply. The need for representative baseline data for water quality parameters, especially as they relate to changes in flow, is obvious and should be considered in developing baseline and operational monitoring programs.

Many states have specific procedures to establish “mixing zones,” which allow for the natural dilution of discharges by stream flow, taking into consideration background levels of individual pollutants and contributions from other dischargers. A mixing zone is a limited area or volume of water where initial dilution of a discharge takes place and where numeric water quality criteria can be exceeded but acutely toxic conditions are prevented (U.S. EPA, 1994d). Mixing zones typically are granted based on low-flow conditions (e.g., the 7Q10 flow in a stream). Since mines often discharge to streams where 7Q10 conditions approach zero, many do not qualify for mixing zones and water quality standards must be met at points of discharge. Operators wishing to use mixing zones must submit an application following procedures outlined in the State water quality standards. Such applications require applicants to work closely with the permitting authority.

States have a wide range of antidegradation requirements that prohibit discharges from degrading existing water quality except under specific conditions. These policies are designed to protect existing instream uses and water quality and to maintain and protect waters of exceptional quality that represent an outstanding National resource. In cases where water quality would be diminished, States are required to assure that water quality would remain adequate to fully protect existing designated uses.

Most State water quality regulations include provisions for developing site- or stream-specific standards and reclassifying (i.e., changing the designated uses of) water bodies. However, there is almost always a significant burden on the applicant to demonstrate the need

for such changes. Operators are encouraged to work closely with States and EPA in determining whether site-specific standards/reclassifications are possible for a site and the supporting information that would be required. EPA must approve all changes to State water quality standards, including site-specific standards and reclassifications.

2.3 Processes that Affect Contaminant Dispersal

The processes that affect contaminant dispersal depend in part on site-specific factors such as climate, geology, surface and ground water hydrology, and water chemistry. These factors control runoff, infiltration, weathering and erosion, and the dissolution and attenuation of metals. One goal of watershed-based analysis is to identify the processes that have a primary controlling influence on water quality throughout the watershed.

2.3.1 Climate

Climatic factors determine seasonal flow in a watershed and affect seasonal infiltration and ground water recharge (see Section 3.3). Changes in infiltration and runoff can impact water quality by affecting the extent to which metals are diluted during downstream flow, the degree to which sediment and metal-bearing particles are eroded and transported downstream, and the impact that may be caused as oxidation products are periodically flushed from waste rock dumps and tailings piles. These effects need to be quantified so that natural and mining-induced contributions to water quality can be distinguished.

2.3.2 Geology

Surficial geology in mineralized areas should be expected to vary at the watershed scale. Variations can be manifested as changes in rock type, depth and character of soils, degree and character of alteration, nature of mineralization, and extent of fracturing. Surface waters flowing over and through different rock and soil types may have different constituent concentrations, particularly with regard to major ions, pH, and alkalinity (e.g., Stumm and Morgan, 1996). For example, where limestone or dolomite are present in a watershed, surface waters may contain significant bicarbonate alkalinity and high concentrations of dissolved Ca and Mg. However, in a different portion of the same watershed that is underlain by granite, waters may have much lower bicarbonate, Ca, and Mg concentrations.

In most mine areas, both the intensity of mineralization and the types of metallic minerals present are likely to change with location in a watershed. Variations in the style of rock alteration (e.g., phyllic vs. propylitic) can cause portions of a watershed to produce surface and ground waters with different water quality characteristics (Smith et al., 1994; Mast et al., 1998). Mountainous terrains may expose the transition from primary hydrothermal sulfide minerals to secondary oxide and carbonate minerals. The different solubilities and acid generating capabilities of sulfide and oxide minerals may produce waters with significantly different pH and metals and sulfate concentrations (e.g., Stumm and Morgan, 1996; Langmuir, 1997). Variations in the intensity and style of fracturing, which should be expected in watersheds that host

structurally controlled mineral deposits, can lead to changes in infiltration, ground water flow, and ground water discharge within a watershed.

2.3.3 *Surface Water Hydrology and Hydrogeology*

A detailed discussion of characterization and measurement of surface water hydrology and hydrogeology is presented in Appendix A, *Hydrology*. Hydrological and hydrogeological processes and their accurate characterization are inherently related to the characterization and identification of potential impacts to important resources such as receiving water quality, aquatic life, vegetation, and wetlands. Watershed hydrology and hydrogeology need to be well understood prior to finalizing a program to characterize receiving water quality. Important watershed characteristics that should be evaluated include peak storm flow, infiltration-runoff relations, sediment load, surface water-ground water exchange, water table elevation, ground water recharge and discharge, aquifer confinement, and the extent of dewatering activities.

2.3.4 *Aqueous Chemistry*

The extent to which receiving waters disperse contaminants through the environment depends partly on water chemistry and soil character (Hutchinson and Ellison, 1991). Under equilibrium conditions, surface and ground waters will acquire constituent concentrations that depend on local physical and chemical conditions, the rate at which secondary phases precipitate from solution, and the tendency for dissolved constituents to sorb onto particle surfaces (Schnoor, 1996). Figure B-1 shows a conceptual physicochemical model of metal transport in a surface water system illustrating the complex interactions affecting concentration. In general, waters with comparatively low pH can retain higher concentrations of metals in solution than neutral waters (Salomons, 1995). Consequently, downstream changes in pH, redox potential, or other chemical parameters (e.g., in mixing zones) can lead to dissolution or precipitation of metal-bearing phases or their adsorption or desorption from bottom sediments or from colloidal precipitates (Oscarson, 1980; Moore et al., 1988; Langmuir, 1997).

The precipitation of colloidal particles is known to be an important process that should be evaluated when assessing water quality (Church et al., 1997; Schemel et al., 1998). Colloids are solid particles with diameters smaller than 1 micron that remain suspended in water due to Brownian motion (particles move as a consequence ionic attraction and molecular collision). Colloidal deposition can occur when particles aggregate into larger masses that can no longer be suspended by molecular forces. Aggregated particles that have settled to the bed of a stream can be resuspended during high flow, causing water quality to decline (Boult et al., 1994). Importantly, most colloidal particles will pass through a 0.45 micron filter and will report as “dissolved” constituents in water quality analyses. Colloidal particles, particularly iron oxyhydroxides, readily sorb dissolved metal ions from the water column (e.g., Chapman et al., 1983; Langmuir, 1997). Although the formation of oxyhydroxide minerals may improve water quality by facilitating sorbtion of other dissolved metal ions, deposition of colloidal particles may degrade aquatic habitat quality by coating substrate materials.

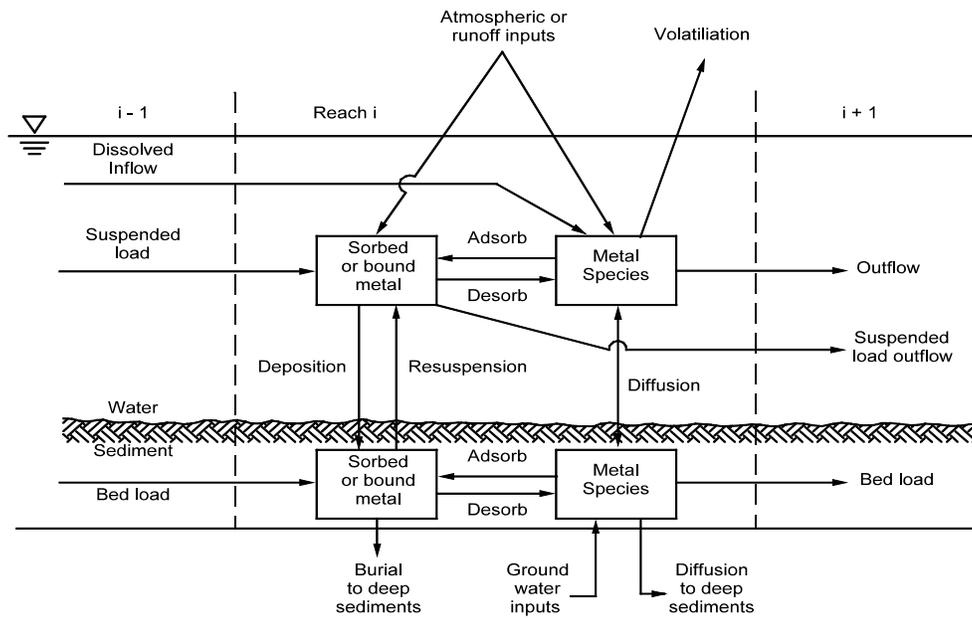


Figure B-1. Conceptual physicochemical model of metal transport in a river from Schnoor (1996).

The stability of colloidal precipitates is a function of chemical parameters such as pH and redox potential. Consequently, chemical changes occurring in a receiving water, such as in a mixing zone, can cause colloidal particles to precipitate or to redissolve and release their adsorbed metal constituents to solution (Church et al., 1997). For example, acidic, metal-bearing water draining an area of quartz-sericite alteration that flows into a stream with significant buffering capacity that is draining an area of propylitic alteration can cause iron- and aluminum hydroxide minerals to precipitate (*cf.*, Chapman et al., 1983; Boulton et al., 1994). Even under natural conditions, water quality in a receiving stream above a mixing zone may have metals concentrations, alkalinity, pH and redox potential that are different from water below a mixing zone (Walton-Day, 1998).

2.4 Using the Watershed-Based Approach

Mine facilities potentially can impact aquatic ecosystems for considerable distances downstream by dispersing contaminants through receiving waters (Salomans, 1995). To anticipate the environmental impact that future mining operations may have and to determine the impact that past and present operations have had on aquatic ecosystems requires an understanding at the watershed level (Hughes, 1985). The utility of the watershed approach recently was recognized in an initiative to remediate abandoned mine lands led by the U.S. Geological Survey (Buxton et al., 1997) and in EPA's Hardrock Mining Framework (EPA, 1997a).

Water quality may vary within a watershed in response to differences in factors such as surficial geology, hydrogeology, infiltration-runoff relationships, seasonal variation, vegetation, land use, and anthropogenic disturbance. As a result, water quality in the downstream portion of a watershed is a mix of the components contributed from each upstream tributary. The watershed-based approach seeks to identify how changes occurring in one or several upstream tributaries impact downstream water quality. It is important to note that the term "watershed" does not necessarily refer to an enormous expanse beyond the reach of the operation. In general, the "watershed" of concern is the upstream portion of a drainage basin that contributes surface and shallow ground water flows to the project area and the downstream portion(s) whose water quality or quantity may be affected by mining-related activities. Under the generally accepted clarification system established by the U.S. Geological Survey, cataloging units appear to be the most appropriate size of "watershed" that may need to be evaluated for the majority of mining projects (see USGS Information Sheet Hydrologic Units, February 1999).

2.4.1 Determining Pre-Mining Background Water Quality

Prior to developing a program to characterize baseline conditions, it is important to recognize the physical variables that may influence water quality in potentially affected watersheds. Among the most important of these are the presence of mineralized exposures, the history and nature of existing disturbances that have caused impacts to water quality, and changes in watershed hydrology. "Natural background" is a term used to describe the water quality of a watershed that has not been disturbed by the actions of man (U.S. EPA, 1997b). In contrast, "anthropogenic background" is a term used to describe the water quality existing in all

or a portion of a watershed that has been disturbed by human actions. The term “baseline” is used to describe the water quality measured at a given point prior to future disturbance and from which departures can be measured. Baseline values may include components of both natural and anthropogenic background.

2.4.1.1 Natural Background in Mineralized Areas

Natural background levels of metals can be high and pH can be low in streams draining watersheds with exposed mineralized rock (Runnells et al., 1992, Bowers and Nicholson, 1996; Mast et al., 1998; Runnells et al., 1998). These characteristics generally are attributed to the weathering and erosion of metal-bearing ores at the earth’s surface (Runnells et al., 1992; Bowers and Nicholson, 1996). In some cases, weathering locally produces streams that are discolored with precipitating metal phases such as ferric hydroxide and zinc carbonate (Runnells et al., 1992). Runnells et al. (1992) compared metals values in stream waters draining areas with exposed metallic mineral deposits to worldwide averages determined for streams draining nonmineralized areas. They found that streams in mineralized areas can have natural pH values of less than 3 and metals values that are 3 to 4 orders of magnitude higher than streams draining nonmineralized areas.

Determining natural background values in a watershed requires knowledge of the geological relationships throughout the watershed, including the distribution, intensity and character of mineralization and alteration, water quality as it relates to natural variations in stream flow, precipitation-runoff relationships, downstream changes in water quality, interactions between surface and ground waters, and the forms in which metals occur in surface and ground waters. For example, variations in the distributions and abundances of metallic minerals will influence the concentrations of metals in surface waters. This is especially true of partially oxidized hydrothermal deposits in which natural weathering processes have converted primary sulfide minerals to variably soluble secondary oxide, hydroxide, or carbonate minerals. Moreover, watersheds in which mineralization occurs in a structurally complex geologic setting may have tributary streams with distinctive water quality characteristics that may be due to the exposure of different rock types in different portions of the watershed. Metals are transported in streams either as dissolved constituents or as suspended particles. The predominance of one form or the other partly reflects the solubility and erodibility of the metal-bearing minerals and the surface water chemistry (e.g., redox state, pH, speciation, adsorptive properties, and degree of saturation). Consequently, changes in stream discharge may have different effects on the concentrations of dissolved and suspended constituents. Typically, increased flow dilutes the concentrations of dissolved metals but increases the concentrations of suspended metals by entraining metal-bearing particles.

The recently documented Red Dog Mine area, located in northwestern Alaska, provides an example of surface waters with naturally high concentrations of metals. The main ore deposit, located in the Red Dog Creek watershed, is a massive lead and zinc sulfide orebody exposed in the upper portions of the Middle Fork of Red Dog Creek sub-basin. Studies conducted prior to mining found that a large portion of the watershed comprising the North Fork tributary was unaffected by the mineral deposit. However, these studies also found that water quality was

degraded in the portion of the watershed downstream of the ore deposit as a result of weathering and erosion of the exposed mineralized rock. Seasonal effects on water quality were apparent. Studies by Dames & Moore (1983) showed that dilution decreased the natural concentrations of cadmium and zinc, which were present primarily as dissolved constituents, as flow increased from snowmelt and precipitation runoff. In contrast, the concentrations of aluminum and lead, which were present primarily as particulates, increased with increasing stream flow because metal-bearing particles were mobilized and carried in suspension by high flows. A clear understanding of the natural background conditions at the proposed mine site proved critical in the preparation of the EIS and NPDES permit for the Red Dog project.

The Red Dog site provides an example of extremely elevated natural background metals concentrations. In most locations, the effects of mineralization on natural background are expected to be much more subtle. Nevertheless, even small departures are important to recognize for the EIS and NPDES permitting processes.

2.4.1.2 Effects of Historic Mining and Other Anthropogenic Disturbances

In many mining areas, historic mining disturbances greatly complicate efforts to determine background geochemical values (Church et al., 1998; Mast et al., 1998). Historic mining activities or other anthropogenic disturbances can alter natural background constituent concentrations in a watershed by disturbing soils and slopes, altering runoff and stream characteristics, and creating mine pits, adits, waste rock dumps, tailings piles, spent leach pads, and other facilities that are sources of metals and other pollutants. These activities lead to increased sediment loads (e.g., by removing vegetation); seeps, runoff, and surface discharges (e.g., from an adit) with elevated levels of acidity and/or metals; and downstream transport and deposition of leachable materials (e.g., tailings solids).

In watersheds with numerous historic facilities, it may be difficult to find surface or ground water sites that have not been affected. A program designed to acquire samples from undisturbed sites may provide data that apply only to the local area or sub-basin from which the samples were collected and not to the entire watershed (Mast et al., 1998). In fact, historic mining disturbances may be so extensive in some areas that it is nearly impossible to fully characterize background values. Runnells et al. (1998) review methods that can be used to determine background at extensively disturbed sites. The most desirable of these is to use historical water quality data. Unfortunately, such data are rarely available or sufficiently complete that they provide an accurate assessment of pre-mining values. Consequently, three indirect methods have been developed to provide some measure of understanding of natural background conditions. One method extrapolates data from an analog site in a nearby undisturbed watershed (Hughes, 1985; Runnells et al., 1992; Bowers and Nicholson, 1996). Such sites must have geological and hydrological characteristics that are similar to those of the watershed of interest. Although analog sites can provide useful data, it is usually difficult to find an exact hydrologic and hydrogeological match (Runnells et al., 1998). A second method uses equilibrium geochemical models to predict the maximum constituent concentrations that can occur in water that is in equilibrium with rock and metallic ore minerals (Runnells et al., 1992; Nordstrom et al., 1996). Geochemical models require that users establish boundary conditions

and make other assumptions (e.g., regarding pH, redox state, etc.) that cannot be easily tested or verified (Runnells et al., 1998). A third method uses a statistical approach to identify the natural background component in water from disturbed areas (Runnells et al., 1998). For example, probability graphs (Stanley, 1987) have been used to identify natural background values in anthropogenically impacted ground waters at the Bingham Canyon Mine in Utah (Runnells et al., 1998). Although statistical methods are capable of identifying multiple concentration populations, the process can become very complicated for areas where surface waters are impacted by numerous mining features. Some of these challenges are described by Moore and Luoma (1990) for the Clark Fork River drainage in Montana.

Church et al. (1998) describe an innovative, indirect approach for determining the extent to which historic mining activities may have affected baseline metals concentrations in a watershed. Their method is to collect and analyze sediment cores from stream deposits formed prior to the onset of mining activities and to compare these values to those obtained from recently formed deposits. In addition to metals and other constituents, sediments can be analyzed for signs of biotic life. This approach provides data only about stream sediment compositions and does not provide direct information on water quality.

In addition to mining, there can be a wide range of other existing disturbances in a watershed that affect water quality. Understanding the effects of all disturbances is essential to producing an adequate characterization of baseline conditions. Depending on the specific setting, this may necessitate collecting samples of runoff and seepage, pore waters, and solids. In some cases, water quality may be controlled by a set of interactive processes that need to be recognized in order to predict future water quality changes. For example, Paschke and Harrison (1995) describe an area of historic mining in Colorado in which metal transport in a stream is affected by ground water interaction and seasonal recharge of a natural wetland. Without such information, it may be impossible to predict and measure the incremental effects of new operations.

3.0 DESIGNING A WATER QUALITY MONITORING PROGRAM

Several factors must be considered when designing and establishing programs to sample and characterize baseline water quality conditions and to conduct long-term water quality monitoring. These factors include: (1) the location of the proposed or existing mine site and its support and waste disposal facilities in relation to the watershed, natural drainages, aquifers, and ground water flow; (2) the location of proposed or existing discharges and expected areas of infiltration; (3) the type of mineral to be mined and the mineralogy of associated waste rock and ore; (4) the type of process chemicals and hazardous materials that will be associated with the operation; (5) the designated uses of all surface waters in the watershed; and (6) the utilization of ground water in potentially impacted aquifers. A complete water quality data set will expedite establishing water-quality-based effluent limits and total maximum daily load allocations, which may be required by a National Pollutant Discharge Elimination System (NPDES) permit (EPA, 1996a).

In general, monitoring programs should achieve the following objectives:

- Define spatial differences in water quality parameters and constituents throughout the watershed.
- Define temporal differences in water quality that result from general changes in seasonal flow.
- Define differences in water quality that can occur during major climatic events, such as low probability storms or droughts.
- Define the effects of mining operations and associated accidental or permitted discharges on water quality.
- Define and monitor the effectiveness of applied Best Management Practices and mitigation measures used by the operation to protect water quality.

3.1 Sampling Locations

A surface water sampling program should define the number and locations of monitoring stations on a watershed basis. Monitoring stations should be established on all major tributaries in a watershed to quantitatively measure spatial changes in water quality that result from variations in geology, soils, mineralization, and land cover and from historic mining operations and other land use disturbances. Existing water quality should be well characterized in potential mixing zones and at downstream points of compliance. Consequently, monitoring stations should be established above and below a proposed or existing mine site and immediately below the confluences of all major tributaries. These locations will provide the types of data needed to define the contributions of different flows to downstream water quality and the water quality changes that occur as two flows mix together. To the greatest practical extent, monitoring stations should be located on straight, hydraulically stable stream reaches that are free of pools and large depositional areas. This will minimize the possibility that samples may vary over time due to streambank erosion, sediment aggradation, and channel (thalweg) migration.

Surface water monitoring stations also should be established above and below permitted discharge points and all hydrologic control structures, such as stream diversions, storm water detention/retention facilities, tailings disposal facilities, or process ponds. These stations are usually required for compliance monitoring. It is important to note that ambient and compliance monitoring programs should be established with common objectives, measured constituents, sampling frequency, laboratory procedures, and detection limits.

Ground water quality monitoring locations should be established in each potentially affected aquifer after considering the lithology and permeability of the aquifer; how, in what direction, and at what speed water flows through it; and whether exchanges occur with surface or other ground waters. Special considerations may be required for shallow aquifers that exhibit seasonal flow in response to spring snowmelt or winter freeze. In general, ground water monitoring requires that data be collected from wells that are located both up-gradient and down-gradient of potential contaminant sources. Existing water quality should be well established in areas that could be impacted by seepage from mine facilities. Numerous publications are available that

describe the design and construction of monitoring wells and provide guidance on programs to monitor ground water (e.g., Nielson, 1991; U.S. EPA, 1993a; 1993b).

Lakes, estuaries, bays, and other tidal areas have unique chemical, physical, and biological characteristics that need to be identified prior to establishing sampling locations. For lakes, this likely will require applicants to complete limnological studies that characterize seasonal biological processes and identify physical phenomena such as temperature stratification, evaporation, degree of mixing, sediment-water chemical exchange, chemical stratification (particularly dissolved oxygen), retention time, and ground water inflow (e.g., Thomann and Mueller, 1987; U.S. EPA, 1990). Additional factors such as tidal currents and temperature, salinity, and density gradients are important in estuaries, bays and other near-shore waters (e.g., Thomann and Mueller, 1987; U.S. EPA, 1992). These types of data are fundamental for establishing sites that will provide representative samples and they form a basis for interpreting the results of water quality analyses.

3.1.1 Mixing Zones

Proposed mixing zones, as defined in Section 2.2, should be characterized as part of the monitoring program. Importantly, mines may be located in areas with highly variable flow conditions that can cause the effects and extent of mixing to change significantly with time. In this regard, water quality immediately above a proposed outfall and mixing zone should be assessed at the time of highest risk. For many dissolved constituents, this typically occurs under conditions of low flow. In contrast, highest risk for constituents carried as suspended particles occurs under conditions of high flow. Developing an accurate understanding of high risk conditions requires that data be collected for as long as possible to adequately characterize seasonal and annual variations in runoff and stream flow that occur in all environments. Applicants requesting mixing zones in lakes, estuaries, bays, or other tidal areas may need to conduct limnological or oceanographic studies that characterize the physical and chemical nature of these environments.

Most States allow mixing zones as a matter of policy, but limit the spatial dimensions of permissible zones. Each is reviewed on a case-by-case basis. State regulations regarding the dimensions permitted for flowing waters (rivers and streams) may differ from those for still-water bodies (lakes, estuaries, coastal waters). Applicants should check with State personnel early in the NEPA and CWA processes to determine the types of data that will be required for a mixing zone application. More information on mixing zones is available in U.S. EPA (1991).

3.2 Sampling Considerations

The data that are used to assess the quality of surface and ground waters form the foundation upon which all interpretations of potential impacts rest. Consequently, it is vital that these data accurately portray water quality. For ambient waters, it may be necessary to use special sample collection and analysis techniques to measure very low concentrations of trace constituents.

3.2.1 Sampling Methods

A variety of techniques can be used to collect samples of flowing or still surface waters and ground water from the vadose and saturated zones. Depending on their intended use, samples may be taken as grab samples, depth integrated samples, composite samples, or continuous samples. Descriptions of sampling techniques and evaluations of the utility of each are not presented herein. Instead, the reader should consult one of the many sources dedicated to these topics such as Hamilton (1978), Canter (1985), Nielson (1991), U.S. EPA (1990; 1992; 1993a; 1993b), or U.S. Geological Survey (1998).

Many EPA analytical methods require that samples be filtered in the field through a 0.45 μm filter. Depending on the constituents that will be analyzed, samples are then treated to prevent precipitation of metal compounds, volatilization of organic constituents, or the production of hydrogen cyanide. These methods are outlined in U.S. EPA (1983; 1986) and briefly described in Appendix C, *Characterization of Ore, Waste Rock, and Tailings*.

Importantly, the quality of trace metal data, especially for metals concentrations below 1 part per billion, can be compromised by contamination that occurs during sample collection, preparation, storage, and analysis. EPA has developed Method 1669 specifically for collecting samples of ambient waters that will be analyzed for trace metals (U.S. EPA, 1996i). The method outlines procedures for collecting, filtering, and preserving samples and field blanks that will be analyzed using low-detection-limit techniques (see Appendix C, *Characterization of Ore, Waste Rock, and Tailings*).

3.2.2 Selecting Parameters

The specific water quality parameters that should be measured by a given operation depend on the site geology, soils, climate, and vegetation; the mineralogy of the mined ore and waste rock materials; process methods and chemicals used in the operation; and the designated uses of and the water quality criteria that apply to the receiving waters. These factors must also be considered when selecting sampling protocols and laboratory analysis procedures. The suite of metals analyzed should be based on knowledge gained from baseline sampling and site geologic studies, including the mineralogy of the ore and waste rock. Table B-2 lists constituents typically measured at metal mining operations.

The adsorptive behavior of metals in water varies as a function of pH and redox potential, and soils have different cation and anion exchange capacities. Due to changes in soil characteristics across a watershed, metals attenuation by soils and sediments will also vary. For these reasons, a mining operation may need to analyze samples for both total recoverable and dissolved metals. These data will help to delineate the chemical behavior of specific metals in the environment and they can be used to define spatial variations in metal loads within the watershed. These data are required to adequately assess impacts to receiving waters that could be associated with an accidental discharge of pollutants.

Table B-2. Water Quality Parameters Typically Measured at Proposed Metal Mining Sites

<u>TCLP Metals</u>		<u>Other Metals</u>	
Arsenic Barium Cadmium Chromium	Lead Mercury Selenium Silver	Aluminum Antimony Beryllium Cobalt Copper	Iron Manganese Molybdenum Nickel Thallium Zinc
<u>Major Cations</u>		<u>Major Anions</u>	
Boron Calcium Magnesium	Potassium Sodium	Ammonia Nitrogen Bicarbonate Carbonate Chloride Fluoride	Hydroxide Nitrite Nitrogen Nitrate Nitrogen Orthophosphate Sulfate
<u>Other Constituents</u>		<u>Other Parameters</u>	
Acidity Dissolved Oxygen Total Alkalinity	Free Cyanide Total Cyanide WAD Cyanide	Conductivity Eh pH Temperature SAR	Total Dissolved Solids Total Hardness Total Suspended Solids Turbidity

3.3 Sampling Schedule and Frequency

Sampling of all monitoring stations should occur at a frequency that permits accurate definition of the changes to water quality that occur seasonally and in response to short-lived changes in flow. Several years of sampling data typically are required to accurately define monthly, seasonal, and annual variations. In general, a sampling schedule should be designed to ensure that water quality data are collected from the range of flows that occur. This will provide a representative set of data that can be used to support NEPA and CWA requirements. Typically programs will need to utilize a combination of periodic and opportunistic sampling. Periodic samples are collected on a regular schedule, for example, monthly. Opportunistic samples, which should be collected throughout the year, are used to define water quality that occurs during extremes in the seasonal hydrograph or during short-lived events. For example, opportunistic sampling should be conducted during high runoff events to determine those parameters that are diluted by high flow (typically dissolved constituents) and those that occur at increased concentrations (typically suspended constituents). Opportunistic sampling also can help to define differences in water quality that occur between high and low stream flow

conditions and to define water quality on ephemeral and intermittent streams. During high runoff events, opportunistic sampling can be used to establish a baseline from which to evaluate the effectiveness of water control structures and BMPs designed to minimize impacts from erosion and sedimentation.

For some locations, applicants may find it useful to link sampling schedules to stream flow as defined by seasonal hydrographs. This approach could prove especially beneficial in watersheds that host a variety of climatic zones due to topographic factors or proximity to coastal waters and in watersheds with severe climates. For example, orographic effects, which cause precipitation to increase with elevation in a watershed, are especially important to consider in coastal and mountainous areas, such as southeast Alaska. Alternatively, mines that are located in mountainous terrain or in northern climates may experience winter periods with extremely low stream flows or freeze-over, followed by periods with excessive runoff during the spring thaw. Mines located in arid or semi-arid areas may experience summer periods with low flow and short periods of intense rainfall that locally produce large discharges. These effects can impact water quality and contaminant dispersal as described in Section 2.3.1.

3.4 Assessing the Health and Diversity of Biota

In addition to characterizing the chemical and physical quality of surface and ground waters, applicants will need to provide an analysis of the health and diversity of biota in receiving waters. These analyses are described in more detail in Appendix G, *Aquatic Resources*. For proposed mining operations, existing streams may be severely impacted by historic activities. Hughes (1985) presents a methodology for determining the health and quality of aquatic life in streams in which this has occurred. His technique relies on identifying control streams in nearby unimpacted watersheds that have similar watershed characteristics to the impacted stream. Control streams are used as analogs from which the potential biotic and habitat conditions of the impacted stream are estimated.

4.0 DATA ANALYSIS

Preparation of Environmental Impact Statements and NPDES permits will require an analysis of water quality and potential impacts that could result from the proposed project. This section describes the types of data analyses that may be required under NEPA and the CWA.

4.1 Contributions of Tributaries and Ground Water to Surface Flow

Applicants may be required to conduct an analysis that constrains the contributions of tributary drainages and ground waters to surface flow. The objective of this type of analysis is to identify whether changes in water quality are related to inflows, particularly in sensitive areas such as proposed mixing zones. Ground water contributions to gaining systems may be especially difficult to assess since the influent sources may not be amenable to direct sampling (i.e., ground water seeps into the stream beneath flowing water). The analysis can be further complicated in historic mining areas located in mountainous terrain where contaminated seepage

flows through shallow soils in response to seasonal climatic changes or short-lived storm events. In cases such as these, the use of dye or salt tracers may provide a clearer understanding of ground water contributions to stream discharge (e.g., Kimball, 1997). Accurate discharge measurements are important for computing metal loadings (Section 4.3).

4.2 Translators for Dissolved to Total Recoverable Constituent Concentrations

Applicants and regulatory personnel may encounter the need to express water quality data in both dissolved and total recoverable (dissolved plus particulate) forms for NPDES permits and Total Maximum Daily Load (TMDL) allocations. NPDES regulations typically require permits to list metals limits in total recoverable form (there are exceptions, so applicants should check with State and Federal agency personnel). On the other hand, EPA may be required to perform TMDL calculations in which metals are expressed in dissolved form to ascertain that water quality standards are being met. Accepted methods for translating between dissolved and total recoverable forms are described in U.S. EPA (1996j).

4.3 Computing Metal Loadings

Constituent concentrations, which are subject to dilution in downstream surface water flows, provide limited information about the behavior of metals in streams. EPA (1996a) suggests that this shortcoming can be overcome by considering metals loads, in which the instantaneous load equals concentration multiplied by discharge:

$$L = C * Q$$

where L is the instantaneous load, C is metal concentration, and Q is stream discharge. The constituent load downstream of a tributary inflow (L_D) is equal to the sum of the upstream loads (L_U) and contributing tributary (L_T) loads:

$$L_D = L_U + L_T$$

(EPA, 1996a). An increase or decrease in load reflects an increase or decrease in the mass of the constituent being transported per unit time. Increases in load along a stream reach can point to sources of contamination that may be recognized (i.e., tributary inflow) or unrecognized (i.e., ground water inflow) during conventional sampling. In contrast, decreases in load suggest that a constituent is being removed by one or more physical, chemical, or biological processes. Physical processes such as sedimentation and sediment transport, chemical processes such as adsorption and colloidal precipitation, and biological processes such as uptake can cause changes in metals loads.

4.4 Other Characterization and Data Analysis Issues

This section briefly describes issues that applicants should be aware of when preparing summaries of water quality data and when analyzing and interpreting historical water quality.

4.4.1 Below Detection Limit Values

Water quality data sets characteristically contain analyses in which some constituent concentrations are reported at values below the method detection limit (MDL). Non-detected values complicate statistical presentations of summary data and can result in statistically unsupported biases being incorporated into summary data presentations. The latter occurs whenever mean and standard deviation values are computed using assumed values (e.g., zero or one-half MDL) for analyses reported as below the detection limit. Further statistical challenges are presented by water quality data sets that include multiple detection limit values.

Computational methods have been developed to deal with data sets containing below detection limit (BDL) values (Gilliom and Helsel, 1986; Helsel and Cohn, 1988; Helsel, 1990; Travis and Land, 1990). In general, these approaches assume that constituent values have a normal or log-normal distribution. Based on this assumption, portions of the distribution reported with BDL values can be reconstructed using either regression order statistics (Gilliom and Helsel, 1986), probability plotting methods (Helsel and Cohn, 1988; Travis and Land, 1990), or maximum likelihood estimations (Cohen, 1959). Extrapolated values are then used to compute mean and standard deviation values for the constituent populations (Helsel and Cohn, 1988; Helsel, 1990). Appendix B of Helsel and Cohn (1988) describes a probability plotting method to extrapolate data sets that include multiple detection limits. The method has gained widespread acceptance for analyzing data with BDL values (e.g., Runnells et al., 1998).

The success with which a substitution method accurately determines the true statistical parameters of a population depends on how closely the data fit an assumed distribution (Helsel, 1990). Bias and imprecision can be introduced whenever data depart from the assumed distribution or when data are transformed (e.g., when means and standard deviations are computed for log-transformed data and then converted back to original units) (Helsel, 1990). Helsel and Cohn (1988) and Helsel (1990) compared root mean square errors of the statistical parameters computed using six methods, including simple substitution for BDL values (e.g., one-half MDL). They concluded that a robust probability plotting method, in which a distribution fit to data above the reporting limit is used to extrapolate values below the MDL, provides the best assessment of population mean and standard deviation. Helsel and coworkers also concluded that percentile values are best estimated using maximum likelihood estimation procedures.

Software to compute summary statistical parameters for data that include BDL values using Helsel's method is available on the worldwide web at <http://www.diac.com/~dhelsel/>.

Simple substitution for non-detected values continues to be widely used and EPA accepts summary data that are prepared in this manner. Most commonly, values of one-half the detection limit are used for non-detected values. However, in cases where numerous parameters are reported as below the detection limit, or where a constituent routinely is not detected, EPA prefers that applicants use techniques that provide the lowest available detection limits.

4.4.2 Using Existing and Historical Data Sets

Water quality data may exist in published and unpublished sources for some mining sites. In many cases, these data can provide valuable insight into water quality prior to, and subsequent to historical land disturbance activities, including historical mining operations. The Agency uses the term “secondary data” to describe data obtained from other sources. Before using such data, the data user needs to determine the reliability or quality of the data. It is often difficult to determine the quality of secondary data because original laboratory reports are not included in published documents and the analyses were conducted prior to the acceptance of standard laboratory protocols (see Appendix C, *Characterization of Ore, Waste Rock, and Tailings*). Interpretations of receiving water quality that are based entirely or partly on existing data should be made cautiously when one or more of the following parameters is unknown: exact sample location, sample collection method, surface or ground water flow, sample preservation, sample handling (chain-of-custody), analytical method, analytical detection limit, and lab accuracy and precision.

It is important for applicants to recognize that secondary data may not have been collected pursuant to a Quality Assurance Project Plan (QAPP), which often leads to problems with its use. In general, applicants should assume that the use of historical or existing data sets, in the absence of a QAPP or other supporting QA/QC documentation, is unlikely to be adequate to support permitting and decision-making on a mining proposal. More detail on quality assurance issues is provided in Section 5.0 of this appendix.

4.5 Geochemical Modeling

The extent to which receiving waters disperse contaminants through the environment depends partly on water chemistry and soil character (Hutchinson and Ellison, 1991). Under equilibrium conditions, surface and ground waters will acquire constituent concentrations that depend on local physical and chemical conditions, the rate at which secondary phases precipitate from solution, and the tendency for dissolved constituents to sorb onto particle surfaces (Schnoor, 1996). Figure B-1 shows a conceptual physicochemical model of metal transport in a surface water system illustrating the complex interactions affecting concentration. In general, waters with comparatively low pH can retain higher concentrations of metals in solution than neutral waters (Salomons, 1995). Consequently, downstream changes in pH, redox potential, or other chemical parameters (e.g., in mixing zones) can lead to dissolution or precipitation of metal-bearing phases or their adsorption or desorption from bottom sediments or from colloidal precipitates (Oscarson, 1980; Moore et al., 1988; Langmuir, 1997). Dissolved metals concentrations also may change through adsorption onto or desorption from the surfaces of soil particles, especially clays (Hutchinson and Ellison, 1991; Salomons, 1995). The adsorptive behavior of metals in water commonly varies nonlinearly as a function of pH due to pH control of precipitation and complexation reactions (Salomons, 1995). Soils have different cation and anion exchange capacities (which measure of the amount of adsorption that can occur) that are a function of the amount and type of clay and organic content (Hutchinson and Ellison, 1991). Due to changes in soil character across a watershed, metals attenuation by soils also is likely to vary.

Geochemical models can be used to determine the stability of phases in aqueous solutions under equilibrium conditions, identify whether metals are likely to be adsorbed onto or desorbed from co-existing solid phases, and calculate the equilibrium composition of natural waters. These programs are particularly useful for understanding how changes in pH can affect metals contents, determining whether metals are likely to precipitate, be adsorbed, or remain as dissolved constituents, and predicting water quality in mixing zones. Brief descriptions of two of the more commonly used models are provided below.

MINTEQA2/PRODEFA2

MINTEQA2 (Allison et al., 1991) is an equilibrium geochemical speciation model for dilute aqueous systems. It can be used to compute the mass distributions between dissolved, adsorbed, and solid phases under a variety of conditions. The software includes an interactive program (PRODEFA2) to create input files. MINTEQA2 can be obtained from EPA's Center for Exposure Assessment Modeling, ftp://ftp.epa.gov/epa_ceam/wwwhtml/minteq.htm.

PHREEQC

PHREEQC (Parkhurst and Appelo, 1999) is designed to perform a variety of aqueous geochemical calculations based on an ion-association aqueous model. The software can be used for calculations of speciation, saturation index, reaction path, and advective transport and to conduct inverse modeling. PHREEQC is available from the EPA Robert S Kerr Environmental Research Lab, Center for Subsurface Modeling Support..

4.6 Fate and Transport Modeling

Numerical chemical fate and transport models are useful for analyzing spatial changes in water quality parameters in receiving waters. In general, fate and transport models employ finite-difference or finite-element techniques to route hydrographs and pollutants through surface water or ground water systems. These simulations couple equilibrium chemical speciation models with physical transport equations to calculate downstream or down-gradient changes in constituent concentrations. These models are especially useful for evaluating the fate and transport of pollutants from point and non-point sources through a watershed. For mining operations, such studies can be used to evaluate and model potential operational releases in conjunction with a NPDES permit application. Brief descriptions of some of the more commonly used models are provided below.

Enhanced Stream Water Quality Model with Uncertainty Analysis (QUAL2EU)

QUAL2EU is a chemical fate and transport model for conventional pollutants in branching streams and well-mixed lakes. The program, which is intended to be used as a water quality planning tool, can be operated in either the steady state or dynamic mode. The software is available on the world wide web through EPA's Center for Exposure Assessment Modeling (ftp://ftp.epa.gov/epa_ceam/wwwhtml/softwdos.htm).

One-dimensional Transport with Inflow and Storage (OTIS)

OTIS is an equilibrium transport model developed by the U.S. Geological Survey that has been applied to small streams in Colorado that have been contaminated by mine drainage (Runkel et al., 1996). The program allows users to subtract the effects of one or more input sources from downstream water quality.

Hydrologic Simulation Program FORTRAN (HSPF)

HSPF simulates hydrologic and water quality processes on pervious and impervious land surfaces, in the soil profile, and in streams and well-mixed impoundments. The operational connection between the land surface and the instream simulation modules is accomplished through a network block of elements. Time series of runoff, sediment, and pollutant loadings generated on the land surface are passed to the receiving stream for subsequent transport and transformation simulation. Water quality and quantity can be evaluated at different segments or outflow points within a watershed. Given appropriate input data and constraints, the model can account for degradation (i.e., decay) or retardation of pollutants. HSPF is available on the world wide web through EPA's Center for Exposure Assessment Modeling, ftp://ftp.epa.gov/epa_ceam/wwwhtml/softwdos.htm.

Finite Element Model Water (FEMWATER)/Finite Element Model Waste (FEMWASTE)

FEMWATER is a numerical ground water model that uses a finite-element solution to solve the governing equations for ground water flow. It can be used to create two-dimensional areal or vertical models as well as three-dimensional models in both saturated and unsaturated media. Because of its numerical approach, it can be used to model transient flow or steady-state flow under anisotropic and layered aquifer conditions. FEMWASTE is a two-dimensional transient model for the transport of dissolved constituents through porous media. Modeled transport mechanisms include convection, hydrodynamic dispersion, chemical sorption, and first-order decay. The waste transport model is compatible with the water flow model (FEMWATER) for predicting convective Darcy velocities in partially saturated porous media. Outputs from ground water fate and transport modeling can be used to develop pollutant input parameters for point or non-point sources to surface water fate and transport models such as QUAL2EU or HSPF. FEMWATER is available on the world wide web through EPA's Center for Exposure Assessment Modeling (ftp://ftp.epa.gov/epa_ceam/wwwhtml/softwdos.htm).

4.7 Other Analysis Techniques

Plots of water quality data can reveal potentially significant changes in constituent concentrations and mass loading that occur downstream through a watershed (spatial trend) or that occur with seasonal changes in discharge at a given point within a watershed (temporal trend). Mass loading profiles (constituent load vs. distance downstream) are particularly useful for identifying reaches of a stream in which metals are being removed by chemical reaction or reaches affected by contaminant inflow (for example, ground water impact in a gaining stream) (Walton-Day, 1998). Mass loading profiles are being used by scientists at the U.S. Geological

Survey to identify and rank contaminant sources and to guide efforts to remediate abandoned mine lands in the Arkansas drainage in Colorado (Kimball, 1997). Plots of constituent concentration vs. discharge or total suspended solids (TSS) for a given sampling point can distinguish elements that are transported as dissolved constituents from those present primarily as suspended particles.

Although not a widely used technology, water quality data are amenable to analysis using a geographic information system (GIS). GIS technology is being incorporated into the U.S. Geological Survey's National Water Quality Assessment Program where it is used to manage large water quality databases and produce graphical data presentations (Qi, 1995; Qi and Sieverling, 1997). At the watershed scale, a GIS can facilitate analysis of spatial variations in water quality and the relationships of water quality to rock, soil, and mine waste compositions.

5.0 GUIDANCE FOR PREPARATION OF A QUALITY ASSURANCE PROJECT PLAN (QAPP)

This section describes the need for and preparation of a Quality Assurance Project Plan (QAPP) for monitoring receiving waters. The section provides an overview of the planning process that is used to develop a QAPP and describes the major components of a QAPP. EPA QA/G-5 Guidance on Quality Assurance Project Plans (EPA/600/R-98/018, February 1998) provides guidance on developing Quality Assurance Project Plans (QAPPs) that will meet EPA expectations and requirements. This document provides a linkage between the Data Quality Objective (DQO) process and the QAPP. It contains tips, advice, and case studies to help users develop improved QAPPs.

5.1 Overview of the Process for Developing a Monitoring Plan

The Agency QA Division recommends the use of a systematic planning process when developing a monitoring program. One such systematic process is the Data Quality Objective Process (U.S. EPA, 1994e). MacDonald et al. (1991) and Dissmeyer (1994) also provide examples of systematic planning approaches that may be applicable to mining projects. Figure B-2, taken from Dissmeyer (1994), is an example of the process used to develop a program to monitor receiving water quality. The two steps most critical to developing a sound plan are to identify specific monitoring goals and objectives and to determine whether the plan, when implemented, meets those objectives. For example, one objective of a surface water monitoring plan might be to define temporal differences in water quality that result from general changes in seasonal flow (see Section 3.0).

Monitoring plans will vary depending on the particular monitoring situation. In general, they include goals and objectives; sampling locations and schedules; a list of water quality parameters that will be monitored and their required detection limits; a brief description of stream morphology at surface water sampling points; sample collection, handling, and analysis procedures; sample transport and chain-of-custody procedures; quality assurance/quality control protocols; and data analysis and reporting procedures.

The time period from mine planning and permitting to reclamation and post-operational monitoring typically is measured in decades. During this time, environmental conditions, mine operations, monitoring requirements, and sampling and analysis protocols are likely to change. Therefore, establishing comprehensive quality assurance and quality control (QA/QC) protocols will help to minimize the impacts of these changes by ensuring that a consistent and accurate approach is used to collect and analyze receiving water data. Implementing these protocols through a written plan will help to ensure that the collected data can be used to evaluate both the short- and long-term quality of receiving waters.

Although there are numerous approaches for ensuring long-term data quality assurance and control, the most common (and often required) approach is the development of a either a Sampling and Analysis (SAP) plan, Quality Assurance Project Plan (QAPP), or both. The SAP and QAPP can be combined into one document, the purpose of which is to establish sound and defensible sampling and analysis protocols that can be used to generate unbiased data with known and traceable accuracy and precision. For the purposes of this appendix, the combined QA/QC document is referred to as the QAPP. The QAPP should be prepared in a manner that promotes acceptance and use by field and laboratory personnel. It should serve as a resource tool and reference manual for all sampling and analytical procedures. The QAPP should be modified when changes occur that significantly alter the applicability or effectiveness of the document.

5.2 Components of a QAPP

The primary elements of an acceptable QAPP include comprehensive discussions regarding Project Management, Measurement and Data Acquisition, Assessment and Oversight, and Data Validation and Usability. Each of these are described in the ensuing subsections. A complete explanation of and prescribed format for all required elements is presented in U.S. EPA (1998c; 1998d). Both documents are available on the world wide web (<http://www.epa.gov/r10earth/offices/oea/qaindex.htm>). Although monitoring programs initially are developed to support decision-making and permitting of proposed mining projects, the formal monitoring programs that are documented in a QAPP can be later used or amended to support other objectives during various stages of a mine life cycle, including operation, closure and post-closure. For example, NPDES permits generally include specific requirements for the preparation of QAPPs to guide collection of water quality data during mine operation. Typically NPDES permits specify that QAPPs adhere to the two guidance documents cited above.

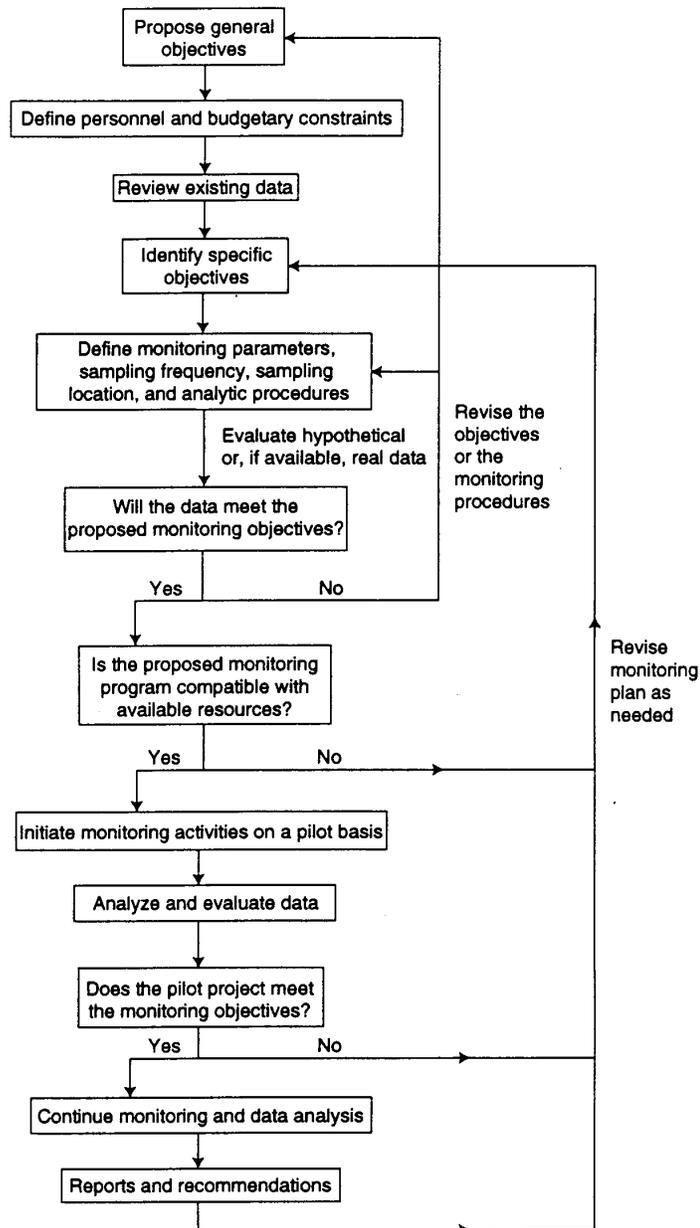


Figure B-2. Example flow-chart for developing a monitoring project (from Dissmeyer, 1994).

5.2.1 Project Management

The project management portion of the QAPP includes an introduction and sections that describe the project schedule, training and certification, expected data quality, and data quality objectives.

Introduction

The introduction should be informative and provide the foundation for solid QA/QC procedures. The section should address plan approval, modification, distribution, and project organization. The introduction should establish procedures for plan modification and identify by name the individuals responsible for project management, overall project quality assurance, field work, and laboratory quality assurance. This should be followed by a detailed presentation of project background information and a brief problem statement. Maps and/or figures should be provided where appropriate.

Project Schedule

An overall project schedule should be developed that highlights key project dates, if applicable. The schedule should be developed in an easily readable format and all project-associated staff should be aware of its presence, content, and key dates.

Training and Certification

The QAPP should address staff sampling and safety training and should include a listing of certifications held by the laboratory. If a commercial laboratory is contracted, it should hold the relevant certifications for the planned analyses from the state where the project is located.

Expected Data Quality

Data quality refers to the level of uncertainty associated with a particular data value (i.e., how sure are you that the value of the data point is what the analysis has determined it to be?). Data quality is affected by all elements of the sampling event, from the sampling design through the laboratory analysis and reporting. Early in the QAPP development process, the acceptable and appropriate levels of uncertainty must be determined through the use of a systematic planning process. Such decisions will depend on the contaminant of concern, the effect it has on human and environmental health, and the levels at which concerns arise.

Decisions regarding acceptable levels of uncertainty should consider the following questions:

- What chemical(s) are expected to be found at the site?
- Approximately what level of contamination is expected (high = >10 ppm; medium = 10 ppm to 10 ppb; low = <10 ppb)?

- What is the action level or level of concern for the contaminant for human health? For the environment?
- Based on the answers to questions 1 through 3, which analytical methods are appropriate to achieve needed detection limits?
- How was the sampling design developed (e.g., area vs. number of samples; frequency of sampling; random or biased sampling)?
- How many of the samples will be field quality control samples (i.e., field duplicates, field blanks, equipment blanks, trip blanks, field spikes or split samples)?
- How many samples will be laboratory quality control samples?

Data Quality Objectives and Data Quality Indicators

After a decision has been made regarding the expected data quality, the QAPP should address data quality objectives and measurement criteria. Data Quality Objectives (DQOs) are quantitative and qualitative objectives that define usable data for meeting the requirements of the project. Data Quality Indicators (DQIs) are specifications for the quality of data needed for the project, such as sample measurement precision, accuracy, representativeness, comparability, and completeness. DQOs and DQIs define the quality of the services required from the laboratory and are used in any quality assurance reviews of the field and laboratory data. Review of the quality control data against the DQOs and DQIs determines if the data are fully usable, considered estimates, or rejected as unusable.

Precision is the degree of mutual agreement between or among independent measurements of a similar property (standard deviation [SD] or relative percent difference [RPD]). This indicator relates to the analysis of duplicate laboratory or field samples.

Accuracy is the degree of agreement of a measurement with a known or true value. To determine accuracy, a laboratory or field calibration value is compared to the known or true concentration. The laboratory, by developing a database of instrument runs using performance samples, should be able provide information regarding this objective.

Completeness compares the data actually obtained to the amount that was expected to have been obtained. Due to a variety of circumstances, analyses may not be completed for all samples. The percentage of completed analyses required will depend on the sampling design and data use. Expectations of completeness should be higher when fewer samples are taken per event or site.

Representativeness expresses the degree to which data accurately and precisely represent a characteristic of an environmental condition or a population. It relates both to the area of interest and to the method of taking the individual sample. The idea of representativeness should be incorporated into discussions of sampling design.

Comparability expresses the confidence with which one data set can be compared to another. The use of standard, published methods allows straightforward comparisons of data collected during multiple sampling events.

Data quality indicators for field and laboratory measurements should be stated in measurement performance criteria. Field measurements should be made with calibrated instruments; laboratory measurements should be specified by individual method criteria or by laboratory control limits.

5.2.2 Measurement and Data Acquisition

The measurement and data acquisition section describes in detail how, where, and when data will be collected and analyzed and provides supporting quality control information related to sample handling; equipment calibration, testing, and repair; analytical methods and quality control requirements; and data management. This section is particularly applicable to all field personnel insofar as it establishes required procedures for sample collection and field measurements. Where possible, information should be presented in tables or other easily understandable formats and should clearly identify prescribed sample locations; maps are strongly encouraged. Tables should be created that list the sample site by assigned identifier (e.g., station 102), common name (e.g., Dry Creek below mill), intended purpose (e.g., assess effectiveness of treatment), and sample types (e.g., pH, flow, turbidity, etc.). The QAPP should provide the reason for including specific sample sites and, where necessary, detailed descriptions of the sample location. Sampling and measurement schedules should be included; tables are recommended in cases where multiple parameters are sampled on varied schedules.

Critical and Non-Critical Samples

In some instances, certain samples may be determined to be less critical than others (e.g., informational samples versus compliance samples). The collection of critical samples may be required at all times, while sampling for non-critical samples may be postponed or excluded based on weather or safety considerations. Criteria for such should be clearly identified.

Sample Collection

Field sampling and measurement procedures should be completely described at a level that would permit a new employee to read and implement these activities without jeopardizing the quality of data. The QAPP should specify methods for collecting different types of samples, using field equipment, and preparing, preserving, and handling samples. In addition, it should present information regarding approved sample containers, preservation methods, holding times, and analytical methods. Proper chain of custody procedures and an example of the form to be used should be provided. The citation and attachment of Standard Operating Procedures to the QA plan can reduce the amount of writing that must be done to properly document the details for a project. For guidance on the preparation of Standard Operating Procedures, refer to U.S. EPA (1995). Field staff should be thoroughly trained on all elements of field sampling and measurement and one or more trial events should be conducted prior to initiating unsupervised sampling.

Analytical Methods and Quality Control Requirements

The QAPP should specify laboratory analytical methods and quality control procedures. A preferred approach is to include a table that presents the analytical methods, method detection limits (MDLs), reporting limits or minimum levels, laboratory precision (in relative percent difference (RPD)) and accuracy (in % recovery), sample holding times, sample container type, sample preservation method, and completeness requirements. The table provides a reference for field teams and allows for easy review of the data deliverables package provided by the laboratory. EPA has established preferred analytical methods for surface water, ground water, soils, sediment, and other media (EPA, 1983; 1986; 1996b-i); other methods are described in APHA et al. (1992) and ASTM (1996) (see Appendix C, *Characterization of Ore, Waste Rock, and Tailings*). Method detection limits are specified in the individual method, while reporting limits or minimum levels are based either upon desired data accuracy and/or regulatory requirements (e.g., NPDES permit limits). Although precision and accuracy guidelines typically vary depending on the specific analysis and/or sample media, <10 to <30% RPD and 85 to 115 % recovery are commonly applied values for water samples.

In addition, the QAPP should specify sample preparation methods and sampling handling procedures as described in the laboratory's QA/QC manual or plan. The lab QA/QC plan or manual should be included with the QAPP as an appendix and pertinent information should be extracted and included in the text of the QAPP.

Field Quality Control

Quality control checks of field sampling procedures and laboratory analyses should be used to assess and document data quality, and to identify discrepancies in the measurement process. Field blanks, equipment decontamination blanks, field duplicates (or replicates), trip blanks, and standard reference samples can be used to assess sample representativeness, sample collection and handling procedures, field equipment decontamination procedures, and laboratory precision and accuracy. Field blank samples, which are used to evaluate whether contaminants have been introduced into the samples by the sampling process, are created by pouring deionized water through a field filter into a sampling container at the sampling point; the field blanks are analyzed for metals and other constituents. In some cases, trip blanks may be needed to evaluate whether shipping and handling procedures introduce contaminants into the samples, or if cross-contamination (e.g., migration of volatile organic compounds) has occurred between the collected samples. Duplicate samples, which are collected simultaneously with a standard sample from the same source under identical conditions and placed into separate sample containers, should be used to assess laboratory performance. One or more duplicate samples should be collected and analyzed for every 20 samples (5%) or once per sampling event, whichever is more frequent. The duplicates should be labeled in a way that does not reveal their status to the laboratory.

Laboratory Quality Control

Laboratories routinely monitor the precision and accuracy of their results through analysis of laboratory quality control samples (EPA Region 10 provides a document for laboratories entitled "Guidance on Preparation of Laboratory Quality Assurance Plans," available on the world wide web at <http://www.epa.gov/r10earth/offices/oea/qaindex.htm>). The QAPP should provide a reference to the specific QC protocols used by the labs that will conduct analyses. The typical frequency specified for laboratory QC samples (e.g., matrix spikes, matrix spike duplicates, method blanks, lab control samples) is one of each QC sample that is appropriate for the method per batch of samples. A batch of samples is defined as 20 or fewer samples that are received by a laboratory within a 14 day period for the specific project. If deemed necessary for the project, a higher frequency of QC samples can be designated.

Corrective Action

If nonconformance with any QAPP element is identified, corrective action should be taken to remedy, minimize, or eliminate the nonconformance. Sampling and measurement system failures include an inability to collect a sample, sample collection errors, field measurement errors, and laboratory errors. The QAPP should prescribe remedies for each of these possible system failures.

Calibration

Field equipment should be calibrated regularly and records should be kept in a field calibration log. The QAPP should include a list of all equipment requiring calibration (e.g., pH meters, DO meters, etc.) and appropriate calibration procedures.

Data Management

Data management requirements should be established for field and laboratory data. They should include acceptable field documentation procedures, laboratory data deliverables, data validation techniques and requirements, data entry, electronic data management, and records retention. The QAPP should present a list of the steps that will be taken to ensure that data are transferred accurately from collection to analysis to reporting. Discussions should focus on the measures that will be taken to review the data collection processes, including field notes or field data sheets; to obtain and review complete laboratory reports; and to review the data entry system, including its use in reports.

Chain-Of-Custody

Chain-of-custody records are used to document sample collection and shipment to laboratories for analysis. All sample shipments for analyses must be accompanied by a chain-of-custody record. Form(s) should be completed and sent with the samples for each laboratory and each shipment (i.e., each day).

5.2.3 *Assessment and Oversight*

The QAPP should adequately describe all monitoring program assessment and oversight. Oversight evaluates how well the specifications contained within the QAPP are being implemented and the types of information needed to continuously improve the monitoring program. It also verifies that the quality assurance guidelines for sampling and analysis are being met. The QAPP should identify the individual(s) responsible for ensuring that sampling and QA activities are being implemented as described in the QAPP. The primary elements of an acceptable assessment and oversight program include audits of field data and sample acquisition, laboratory audits, and audits of data management.

Audits of Field Data and Sample Acquisition

Data quality audits assess the effectiveness and documentation of the field and laboratory data collection processes. In particular, these audits evaluate whether the DQOs established for the project are being met. Additionally, they determine whether the QAPP is still applicable to the current project. The frequency of these audits, which may range from daily to annually, depends on the scope and complexity of the monitoring program. The audit should be performed by someone who is not associated with the day-to-day implementation of the monitoring plan.

Laboratory Audits

A review of the laboratory facility, its equipment, personnel, organization, and management, evaluates the reliability of the data produced by the laboratory. The laboratory, as a system, is verified against the documentation provided in their QA manual and standard operating procedures.

Data Management Audits

Data management reviews evaluate whether the standard procedures in the QAPP are being followed and if the integrity of the data is being maintained. Audits should be conducted at least every other year, but may be conducted more frequently if needed.

5.2.4 *Data Validation and Usability*

This section of the QAPP states the criteria for deciding whether a data element has met its quality specifications as described above. Data validation is the process by which data are compared with DQOs to determine which data points are accepted, rejected, or qualified. The data validation and usability determination evaluates sampling design, sample collection procedures, sample handling, analytical procedures, quality control, calibration, and data reduction and processing.

Validation and Verification Methods

Upon receipt from the laboratory, data should be compared with the specified DQOs and analytical methods. Corrective actions should be selected to prevent or reduce the likelihood of future nonconformances and, to the greatest extent practical, address the causes of nonconformance. Prescribed corrective actions should already exist in the QAPP and these should be implemented first. Future audits should ensure that similar errors do not recur.

Reconciliation with DQOs and DQIs

The QAPP should clearly identify the actions that will be taken to reconcile any deviations from the DQOs and DQIs. Resolution should be made by identifying the elements of the sampling and data collection process that are in question and addressing the situation that caused the qualification.

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